Development of Electrically Conductive DLC Coated Aluminum Substrate for the Advanced Electric Storage Devices by Plasma Ion Assisted Deposition Method

Masayasu Tanjyo and Yasuo Suzuki

October 9, 2018

Development of Electrically Conductive DLC Coated Aluminum Substrate for the Advanced Electric Storage Devices by Plasma Ion Assisted Deposition Method

Masayasu Tanjyo, Yasuo Suzuki

Plasma Ion Assist Co.,Ltd *Nakagawara 34-1, Kamitoba Minami-ku Kyoto, Kyoto, 601-8142 JAPAN*

E-mail; m.tanjo@plasma-ion.co.jp

Abstractð

This paper relates to the development of electrically conductive DLC coated Aluminum(Al) substrate for the advanced electric storage devices by Plasma Ion Assisted Deposition(PIAD) method. Due to its low contact resistance and high corrosion resistance capability the electrically conductive DLC coated Al substrate is confirmed to be useful as the electrode material of the electric storage devices such as EDLC, LiC, LiB, especially for the increase of the cell voltage.

Keywords—conductive, DLC, resistance, corrosion, electric storage device

I. Introduction

1-A. Diamond like Carbon Material

A diamond-like carbon (DLC) film is a material positioned between diamond and graphite. When DLC is coated on the surface of the steel material, the coefficient of friction is reduced to 1/4 and the abrasion resistance is dramatically improved. In addition, the amorphous DLC film containing hydrogen has toughness, and when coated on plastics, it has the property of not passing oxygen and water. Utilizing these characteristics, the application market as a low friction / wear-resistant member of mechanical materials, tools and electronic devices, and as a gas barrier coating of PET bottle is greatly expanding. Since the raw material is carbon, it has environmental harmony, and the scope of application of DLC seems to expand further in the future.

On the other hand, as shown in the application for the electrostatic protection or electrical contact material, DLC also have the electrical property and is used in the electrical field. However, it does not look like it is tightening a big market on an industrial scale.

We have been promoting development of electrically conductive DLC for a fuel cell separator [1] . And we have verified the possibility of reducing the resistance and improving the corrosion resistance by depositing electrically conductive DLC on the Al substrate as the electrode of the electric storage device,under support of AIST.[2]~[6] As is well known, these market is in widespreading today.

1-B. Electric Storage Device & its Market

Recently, the new electric storage devices which equips on the Electric Vehicles (EV); Electric Double Layer Capacitor (EDLC), Lithium Ion Capacitor (LiC), Lithium Ion Battery (LiB) were developed. Figure 1 compares those devicesô power density (W / kg) and energy density (Wh / kg) per kg. Depending on the electrode materials, LiC has a high power density and the high instantaneous current, and LiB has a high energy density and the long operation life time. EDLC has a intermediate performance of them[7]. Among them, LiB has the largest market size, which is divided into the mobile phone batterie, the stationary power batterie, and the automotive batterie. The automotive batterie market is the biggest now and the highly rise rate.

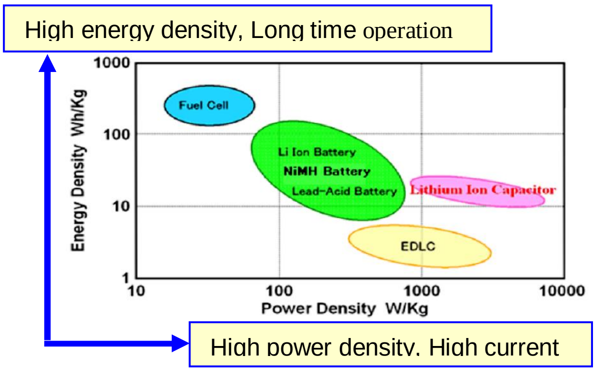


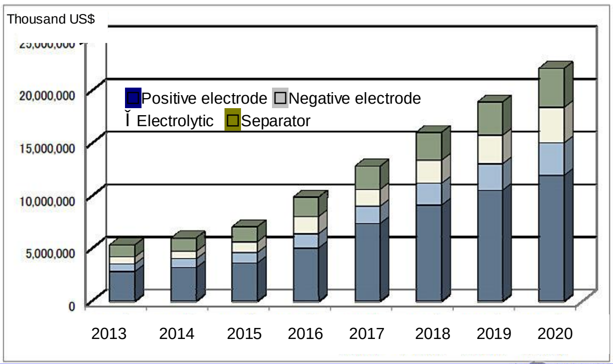
Fig.1 Electric Storage Family; EDLC, LiC, LiB

In Fig.2 it is shown the main compositions of the positive / negative electrode, separator and electrolyte of the electric storage devices. Since EDLC does not use the reactive Lithium, it can be said the most secure.

Electric Storages	Negative Electrode	Positive Electrode	Separator	Electrolyte
EDLC	Activated carbon	Activated carbon	Insulation films	NaPF6-in Dimethoxyethane (DME)
LiC	Carbon	Activated carbon	Nonwoven fibers, polymer films	non-aqueous LiPF6 etc.
LiB	Carbon, LTO etc	Lithium oxide, LiNiCoMnO2	Nonwoven fibers, polymer films	non-aqueous LiPF6 etc.

Fig.2 Electric Storage Devices ; Structure of EDLC, LiC, LiB

In Fig.3, it shows the trends in market size of each constituent electrode material. The total market size of 10.2 B $ in 2016 has doubled to 22.5 B $ in 2020, which shows that it is growing at a rate of 17% per year. It is said that it will further expand after 2020. Expansion of the market size as described above constitutes the front and back of the technology development of the product, and it is necessary to achieve the main theme for improvement of the electric storage device.



・LiB market: 10.2B$ @2016 ⇒ 22.5B$ @2020 CAGR +17%(2016-20)
・P-E material: N-E material: Electrolyte: Separator
= 11.4: 3.5: 3.8: 3.8 (B$) @2020

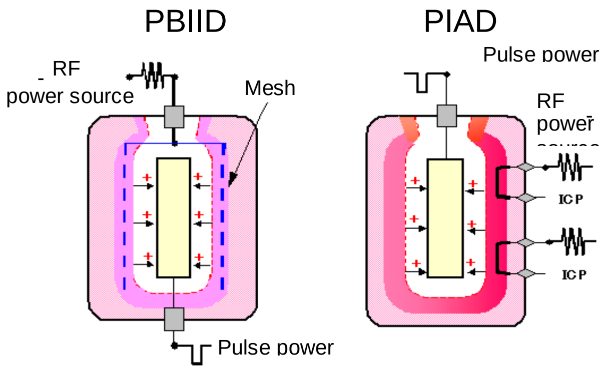
Fig.3 LiB major 4 materials world market size [8]
(Positive electrode, Negative electrode, Electrolytic, Separator)

III. Method and Equipment

A. PBIID vs.PIAD deposition method

There are some kinds of DLC film formation methods, one is the arc-ion plating another is the sputtering. But those films are basically porous because DLC film consists of large size carbon particles. Therefor it cannot be avoided to be inferior to corrosion resistance. In method of developed PBIID [2]～[6] technology (Plasma Based Ion Implantation and Deposition), which ionizes the Methane and the Acetylene gas simultaneously by applying RF and high pulsed voltage, the carbon ion is implanted and deposited on the substrate, and electrically conductive DLC film is formed. This film is porous free and superior to corrosion resistance.

On the other hand, PBIID has two methods, CCP (Capacitively Coupled Plasma) and ICP (Inductively Coupled Plasma). Figure 4 shows comparison of two methods. Feature of ICP method is that plasma density is very high and deposition rate is very fast. The Acetylene gas are ionized by simultaneously applying RF and high pulsed voltage, carbon ion is implanted and deposited to substrate, and electrically conductive DLC film is formed, which is called PIAD (Plasma Ion Assisted Deposition) method.



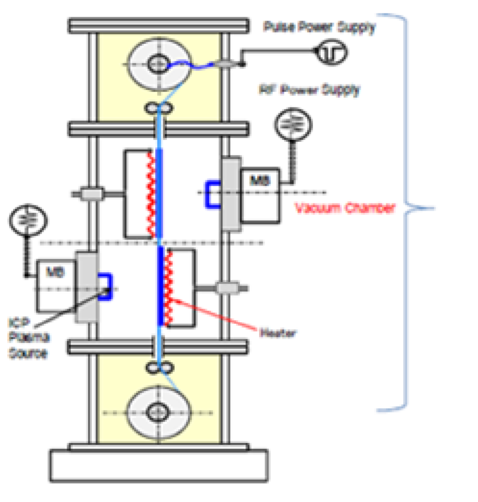
No.	PBIID	PIAD
Plasma	13.56M-CCP	13.56M-ICP
structure RF-Power source	Flat plate /Cylindrical mesh	One turn Coil
Plasma density	～3E10/cm3	～3E11/cm3
Plasma uniformity	±10%	±10%
Deposition speed	1 μm/h	5 μm/h (※)

※The RF power is 3kW.

Fig.4 Comparison of PBIID vs. PIAD methods [1]

B. R to R DLC Coating System

In Fig.5, it is shown the Roll to Roll coating system which makes high throughput with both-sides PIAD plasma coating. The aluminum substrate roll is set on the above vacuum chamber and flows into the plasma processing chamber with heating and then the substrate is rolled up at the below vacuum chamber.



Plasma	ICP
ICP source structure	One turn coil
Plasma density	～3E11/cm2
Plasma Uniformity	±5%
Roll speed	～15cm/min

Fig.5. Structure and Spec of Roll to Roll Equipment

II. Diagnostics and Measured Results

A. Contact Resistivity

The contact resistance has a unit of q cm 2 as a physical quantity obtained by converting the potential difference when electric current passes through the surface touched by a dissimilar substance into resistance. Since the contact surface in usually is not flat that the contact area is smaller than apparent, and the current density in the contact surface is actually large. The contact resistance is a resistance value considering the effective contact surface and can be evaluated by the heat generation $W = I^2 Rs$ at the contact-surface.

In the case of an electric storage device, since the contact resistance between the DLC film formed on aluminum and the electrode active material is the object, evaluation is made by direct contact resistance between the case where the carbon paper(GDL), as substitution of activated carbon, is sandwiched and the gold, which are shown in Fig.6.

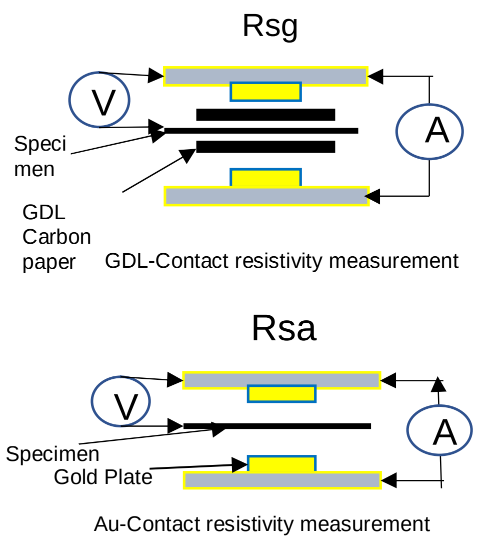


Fig.6 Contact Resistivity Measurement

B. Contact Resistivity vs. Heat Temperature

In Fig.7.it is shown the typical result of contact resistivity vs. heat temperature at the experimental conditions. It is shown the high temperature makes low resistivity.

・Coating Condition: Pulse Voltage : ～1kV, Pressure : ～1Pa, Gas : ～C2H2

No	1	2	3
Heater Temperature(℃)	200	300	400
Rsg（mq cm2)	292	134	70.9
Rsa（mq cm2)	6.4	0.407	0.215

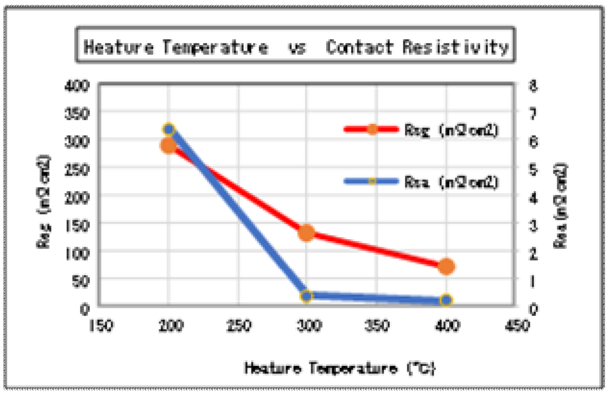


Fig.7 Contact resistivity and heat temperature

The contact resistivity Rsg and Rsa show decrease with the heater temperature, which is caused from the contact surface micro-configuration and the DLC crystalline composition.

C. Corrosion Resistivity and Leak Current

In Fig.8, it is shown the anodic polarization curve with electrically conductive DLC for Al substrate.

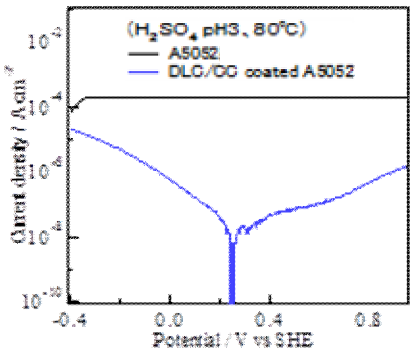


Fig.8 Leak current measurement of DLC film for Al substrate

Even in the severe corrosion resistance test in concentrated sulfuric acid, compared with the uncoated substrate leak current of 2E-4A/cm2, coated one is 7E-7A/cm2 at 0.65V. Only a very weak current of about 1/300 or less flows. It is understood that the electrically conductive DLC film has high denseness and is excellent in conductivity as well as corrosion resistance.

D. Hydrophilicity

Fig.9 shows the results of evaluating the property of imparting hydrophilicity by plasma treatment after DLC coated Al film with a contact angle. Without the treatment, the contact angle is 70 degrees, indicating hydrophobicity, but it shows hydrophilicity at a contact angle of 30 degrees or less by the treatment for about 2 minutes. As a result, the adhesion of the slurry can be improved, which is effective for reducing the circuit resistance.

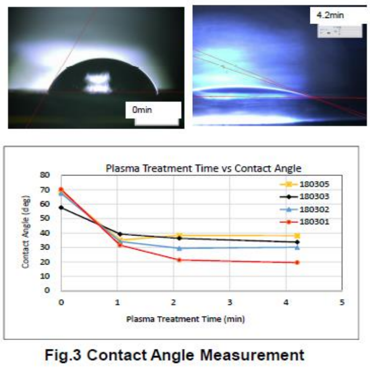


Fig.9 Surface Treatment by O2 for Hydrophilicity control, gives surface hydrophilicity which makes high contact of slurry of activated carbon.

IV. ELECTRIC STORAGE CELL EVALUATION

A. Cell Impedance and Rate Discharge test

It shows in Fig.10, the DLC coated Al cell resistance is 0.3Ω, that of non-coat base Al is 2.4Ω, and that of the usual etched Al is 0.6q which is 1/2 lower resistance. After the rate discharge of 500C the rate retention of 92.5% means suitable for the EDLC cell.

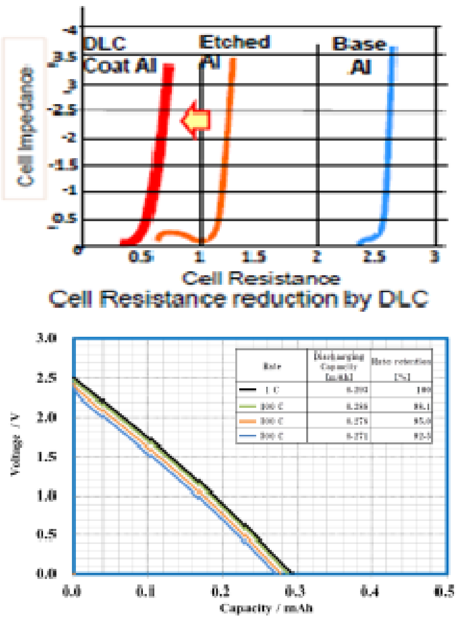


Fig.10 Cell Impedance and Rate discharge test results

B. Withstand Voltage Test by DLC coated EDLC Cell

EDLC Cell for evaluation: Heater Temp 400 ℃ DLC coated Al substrate.

①withstand voltage test by EDLC Cell

②Leak Current test . test temp：60℃

applied voltage: 2.7VŸ 2.9VŸ 3.1VŸ 3.3V ,

and 3.1 V /5 hours charging +100 hours hold voltage.

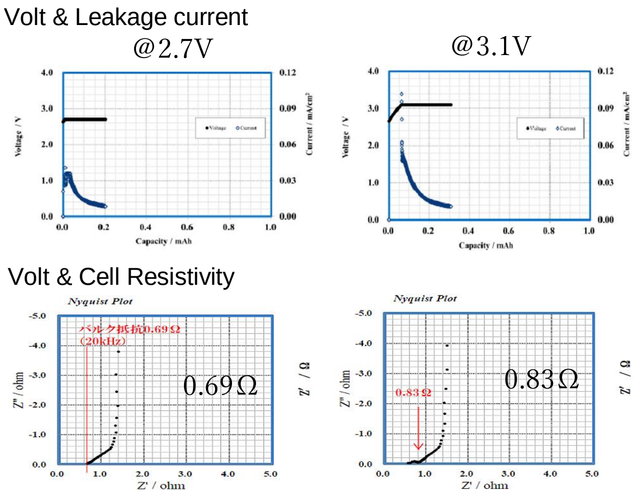


Fig.11 Applied voltage vs. leak current and resistivity for EDLC DLC Cell

It shows, DLC coated EDLC Cell have a 3.1V and more withstand voltage. As the energy density is direct conecting with the withstand voltage Vws that,

$$Ed \propto Vws^2 \Rightarrow (3.1V / 2.7V)^2 = 1.3$$

Energy density increases to 1.3 times.

V. CONCLUSION

- Electric storage device such as LiB, LiC, EDLC recently big expand for the market of the EV, which requires high energy, high current, high safety and low cost.
- Experimental results of electrically conductive DLC of PIA applied to the EDLC cell shows higher operation voltage of 2.7V to 3.1V, higher corrosion resistivity of leakage current 2E-4A/cm2 to 7E-7A/cm2, and lower circuit resistance of 0.6Ω to 0.3Ω.
- Requirement of the electric device of high energy asks high voltage operation with high corrosion resistivity and low circuit resistance, it is confirmed that the electrically conductive DLC of PIA has the solution potentiality for those requirements.

ACKNOWLEDGMENT

The authors would like to acknowledge to PIA staffs of Dr.M.Watanabe, and Mr.Y.Kanamori for their valuable suggestions and Mr.G.Fukumoto for his experimental operation. This work was supported by the Support Industry Program of Kinki Economy Industry office, funded by the Japan Ministry of Economy, Trade and Industry.

REFERENCES

[1] Y.Suzuki, M.Watanabe, T.Toda, T.Fjii, *J. Phys.: Conf. Ser.* 441 012027.(2013)

[2] Conrad J R, Radtke J L, Dodd R A, Worzala F J, and Ngoc C Tran 1987 *J.Appl.Phys.* **62 No.11** 4591-4596

[3] Y.Suzuki 1998 *OYO BUTURI*, **67 No.6** 663-667

[4] Y.Suzuki 2002 *JIEED Japan* **45 No.2** 30-35

[5] Y.Suzuki 2003 *IEEJ Trans.EIS.* **123 No.1**

[6] Y.Suzuki 2006 *JIEED Japan* **49 No.2** 41-46

[7] JM Energy http://www.jmenergy.co.jp

[8] "//www.googletagmanager.com/ns.html?id=GTM-5TVS6ò